Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 83 (2014) 403 – 406

Procedia Engineering

www.elsevier.com/locate/procedia

"SYMPHOS 2013", 2nd International Symposium on Innovation and Technology in the Phosphate Industry

Composite material with calcium sulfate and calcium phosphate for heavy metals retention

Nacira Belaicha[a], Wahiba Lemlikchi[a], Med Oimar Mecherri[a], Patrick Sharrock[b]*, Ange Nzihou[b]

[a]*Laboratoire LCAGC, Faculté des Sciences, Université de Tizi-Ouzou, DZ-15000, Algérie*
[b]*Université de Toulouse, Mines Albi, CNRS, Centre RAPSODEE, Campus jarlard, F-81013 Albi cedex 09, France.*

Abstract

Porous composite materials containing calcium phosphate and calcium sulphate were elaborated by mixing various hydroxyapatites with calcium sulphate hemihydrate, adding water and moulding the paste into shape. The composite material was broken into small granules of 5 mm size to test for heavy metal retention in a column configuration. It was found that the amount of zinc ions retained depended on the contents in apatites present in the composite, and that results were similar to the results obtained for equivalent amounts of pure apatite put in the same column. These results are interesting because previous work on pure apatites showed release of small sub-micrometer sized metal phosphates when the apatite particles were contacted with heavy metals in a flow-through experiment. Thus, the plaster matrix does not prevent metal uptake from aqueous solutions and helps minimize release of fines from the used apatite. The breakthrough curves and zinc retention capacities will be presented for various composite compositions, flow rates and zinc concentrations.

Peer-review under responsibility of the Scientific Committee of SYMPHOS 2013

Keywords: hydroxylapatite, plaster, composite, lead, zinc, metal sorption .

1. Introduction.

In a previous communication [1], we described the formation of a composite material based on hydroxylapatite inserted in a calcium sulfate porous hybrid material, herein named composite. It was found that hydroxylapatite could be incorporated up to 30% by weight without significant deterioration of the mechanical strength of the composite and that the porosity was sufficient to allow for fluid flow. Calcium sulfate and phosphate composites have been reported before [2] and found to have good water resistance. Such composites have been described for use as resorbable biomaterials in bone surgery [3], but have never been used for the retention of heavy metals from polluted waters. Here, our objective was to test the composite for heavy metal uptake and compare the result with the well-known capacity of pure apatites to sorb metal ions. The composite materials were tested both in batch mode and in a column continuous flow-through mode.

* Corresponding author. Tel.: +33 5 63 62 11 59
E-mail address: patrick.sharrock@iut-tlse3.fr

Peer-review under responsibility of the Scientific Committee of SYMPHOS 2013
doi:10.1016/j.proeng.2014.09.048

2. Experimental

The composites were made as described previously [1], namely by mixing the calcium sulfate hemihydrate with determined amounts of calcium phosphate and adding enough water to make a soft paste that could be placed in a mold and left to harden. Afterwards, the composite was unmolded and tested for mechanical compression strength, and the broken pieces of composite were sieved to recover the fragments of 1 to 3 mm diameter sizes. These particles were used as such in batch experiments in contact with lead or zinc nitrates, or placed in a glass column in contact with lead or zinc nitrate solutions of determined concentrations flowing through at selected flow rates. The metal ion solutions had a concentration of 100ppm of metal each (Pb and Zn). The solutions exiting from the columns were sampled every 10 mL for analysis by atomic absorption for metal ions concentrations.

3. Results and discussion

The first few mL of solutions coming out of the columns had very low metal ion concentrations, showing that the lead or zinc ions were effectively removed from solution by the porous composite particles. Fig.1 illustrates the % metal adsorbed on 1.5 g of porous hydroxylapatite derived from duck bones for the case of zinc flowing at a rate of 4mL/min., and shows that the amount removed from solution decreased rapidly as the flow of solution rose above 20 or 30 mL. The breakthrough point is very close to the first volume of solution penetrating the particles. The result shows that the fast initial sorption was followed by continuous but slower sorption up to 200 mL. The consecutive amounts of metal removed stabilized near 0.6 mg of Zn per g of hydroxyapatite and explains the slow decrease in the cumulative percentage of metal sorbed.

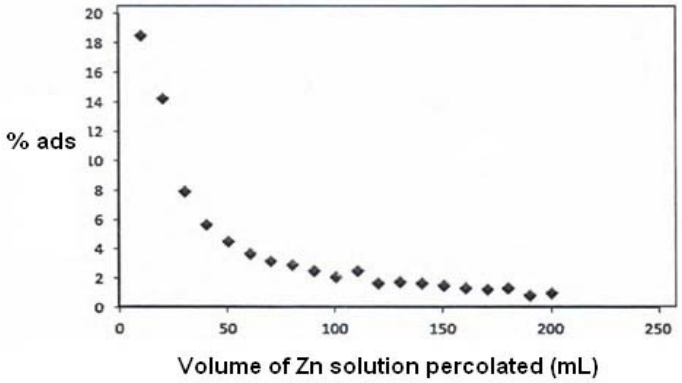

Fig. 1. Plot of the % of zinc adsorbed as a function of the volume of zinc solution percolated.

The value for pure HA are lower than those observed for porous spongy duck bones [4], and explained by the lower specific surface areas of the synthetic counterparts.

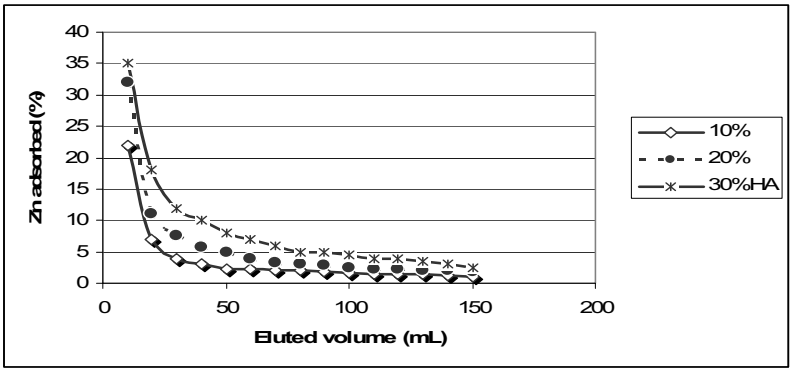

Fig. 2. Plot of the % of zinc retained versus percolation volume (mL)

Fig.2 illustrates the corresponding output profiles for the same conditions (4mL/min), but for the composites in columns containing various composite amounts to correspond to the same amount of apatite as in figure 1 (1.5 g). The curves show the composites for 10, 20 and 30% apatite in plaster and reveal that the more apatite is enclosed in plaster, the higher is the amount of metal retained. The weights of zinc sorbed were found to average 0.12mg/gcomposite at 10 or 20% apatite contents, and 0.28mg/gcomposite at 30% apatite contents. In the case of composites made with 10, 20 and 30% synthetic apatites, the Zn amounts sorbed were found to be near 0.06, 0.07 and 0.08 mg/gcomposite.

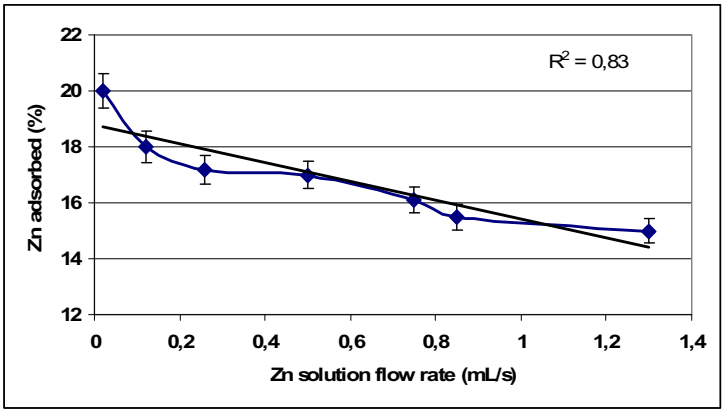

Fig. 3. Plot of the concentration of captured zinc versus entering zinc concentrations.

Fig.3 shows the slight decrease in the % of Zn adsorbed as a function of flow rate, illustrating the fact that faster flow results in less metal ion capture, as expected when the solution has less time to equilibrate with the sorbent. The linear regression line does not fit very well the experimental points (R2 = 0.83) because the flow rates were difficult to keep constant.

Figures 4 and 5 relate to the case of lead ions, and show that higher initial lead concentrations correspond to more lead sorbed (Fig.4), and that the cumulated % sorbed decreases as a function of lead concentration (Fig.5). In this case, the concentrations coming in were compared to the concentrations coming out to deduce the concentrations sorbed.

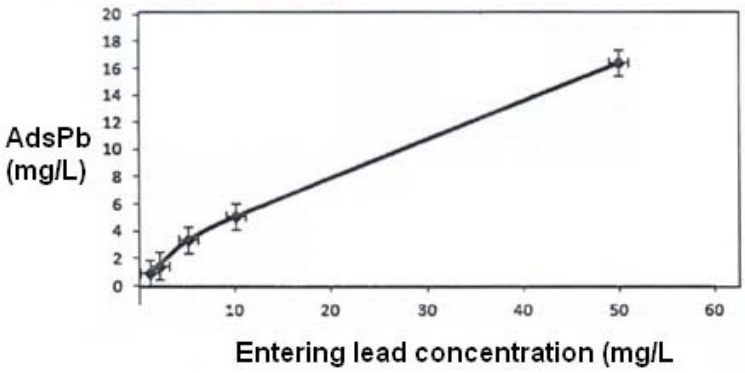

Fig.4. Plot of the concentrations of lead ions removed as a function of entering concentrations

This means that at the flow rate used the composite saturates above lead concentrations over 10mg/L, which results in lower removal rates. Figure 6 details the concentrations removed as a function of the flow rates for 3 different lead ion concentrations. Again, higher incoming concentrations correspond to higher concentrations sorbed, and faster flow rates lead to lower concentrations sorbed.

In the case of batch experiments using lead ions with various solution to solid ratios, similar pH values were found (pH value of 6) following the addition of the solids (hydroxylapatite or composites) to the initial lead solutions (pH values between 3.5 and 5.0), showing the buffering capacity of hydroxylapatite, pure or in composite form.

With daily agitation, the total amounts of lead removed from solutions reached 1glead/gsolid sorbent following 4 days, whether the sorbent was pure apatite or composite material. This shows the high retention capacities of the composite materials. The retention mechanism for heavy metals may be explained by an exchange of the calcium ions in apatites with the lead or zinc ions in solution, as has been proposed earlier for pure hydroxyapatite sorption experiments [5,6]. Few reports exist on the use of apatite in composite materials for heavy metal retention [7,8]

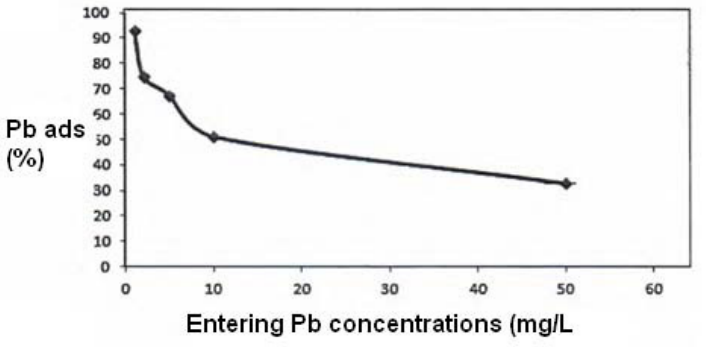

Fig. 5. Plot of lead adsorbed versus entering lead concentrations

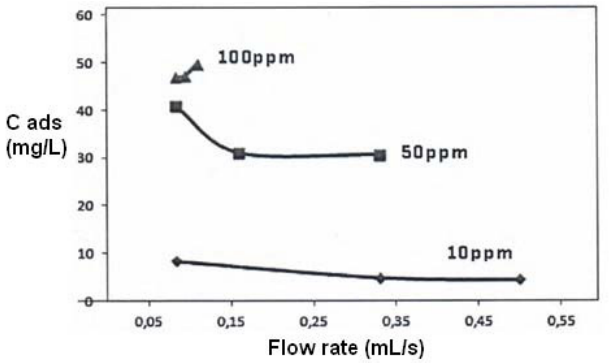

Fig.6. Concentrations of lead adsorbed versus solution flow rate

4. Conclusion

Porous plaster particles containing hydroxyapatites are capable of retaining zinc or lead ions from aqueous solutions in a fashion related to the equivalent amount of free hydroxylapatite. The composite formulations allow incorporating specific amounts of porosities or apatite contents adapted to treat different pollution cases. The release of soluble components remains to be evaluated in order to fully characterize the properties of the composite materials.

References

[1] N.Belaicha et al, Symphos 2013, preceeding paper.
[2] Robin D. Fisher, John V. Hanna, Gregory J. Rees and Richard I. Walton, Calcium sulfate-phosphate composites with enhanced water resistance, J. Mater. Chem., 2012, 22, 4837-4846.
[3] Nathan Evaniew, Victoria Tan, Naveen Parasu, Erik Jurriaans, Karen Finlay, Benjamin Deheshi, Michelle Ghert, Use of a Calcium Sulfate–Calcium Phosphate Synthetic Bone Graft Composite in the Surgical Management of Primary Bone Tumors, Orthopedics, 2013, 36 (2)216-222.
[4] Eric Deydier, Richard Guilet, Patrick Sharrock, Beneficial use of meat and bone meal combustion residue: “an efficient low cost material to remove lead from aqueous effluent”, Journal of Hazardous Materials, 2003, 101, 55–64.
[5] Baillez S., Nzihou A., Bernache-Assolant D., Champion E., Sharrock P., “Removal of aqueous lead ions by hydroxyapatites: Equilibria and kinetic processes”, 2007, Journal of Hazardous Materials, 139, (3), 31 pp 443-446.
[6]Hadioui, M.,Sharrock, P.,Mecherri, M.O., Brumas, V.,Fiallo, M., “Reaction of lead ions with hydroxylapatite granules”, 2008. Chemical Papers 62 (5) pp. 516-521.
[7] M. Hadioui. Synthèses d’hydroxyapatite et de silice greffées pour l’élimination de métaux toxiques en solution aqueuse. Thèse de doctorat.Université Paul Sabatier. France. (2007).
[8] Hadioui, M., Mecherri, M.O., Sharrock, P., Silica gel and hydroxyapatite composites with ormosils for heavy metal removal from water, 2006 AIChE Spring National Meeting - 5th World Congress on Particle Technology; Orlando, FL; United States;(2006) Code 74097.